Journal of Analytical and Applied Pyrolysis 93 (2012) 63–67

Contents lists available at SciVerse ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Preparation and fuel properties of biochars from the pyrolysis of exhausted coffee residue

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ARTICLE INFO

Article history:
Received 24 January 2011
Accepted 20 September 2011
Available online 29 September 2011

Keywords:
Exhausted coffee residue
Pyrolysis
Biochar
Fuel property
True density

ABSTRACT

Exhausted coffee residue (ECR), a processing by-product from the soluble coffee industry, was evaluated as a potential feedstock for preparing biochar fuel. Its thermochemical characteristics were first investigated using the standard methods, showing that the biomass obviously comprises a large percentage of volatile matter and less amount of ash. Its molar ratio of hydrogen to carbon (H/C) is about 1.59, which is close to the cellulose (H/C = 1.67) and hemicellulose (H/C = 1.60). Under the pyrolysis temperature of 673–973 K and the heating rate of about 10 K/min studied, the yields and calorific values for the resulting biochar products reached to the maximum at the condition of around 673 K. The calorific value (around 31.9 MJ/kg) of the optimal biochar from ECR was relatively high as compared to that of coal. However, the resulting biochar has greater nitrogen content, which may contribute to greater nitrogen oxides (NO_x) emissions during combustion or co-firing. On the other hand, the resulting biochars were characterized using helium-based solid density (true density), showing that the density increased with increasing pyrolysis temperature in accord with the conversion of low-density disordered carbon to high-density turbostratic carbon.

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1. Introduction

The reuse of renewable bioresources as energy sources or alternative fuels in replacement of fossil-based feedstocks has received much attention in recent years. This transition from nonrenewables to renewables is mainly due to the energy crisis and environmental issues (e.g., global warming). The energy supply from domestic biomass resources not only enhances fuel diversification, but also reduces the air pollution because the biomass resource contains relatively low contents of sulfur and heavy metals in comparison with fossil fuels such as coal [1]. In this respect, agricultural residues contain large amounts of lignocellulosic constituents (i.e., cellulose, hemicellulose and lignin) and thus possess high-energy contents [2]. Therefore, they can enrich available carbon sources in the production of biomass energy based on benefits of both energy utilization and environmental protection. For these reasons, there is an increasing interest in co-firing biomass with coal in the power plants and industrial utility boilers [3], which have been designed with the best available control technologies for hazardous or toxic air pollutants emitted from flue stack. However, the success of coal co-firing was limited to about 20% biomass mix mainly due to the contents of moisture, ash and chlorine in the biomass [3].

Coffee is one of the most important agricultural commodities in the world because it is a popular brewed drink prepared from roasted bean. However, the processing of coffee often generates significant amounts of solid residues. Among them, exhausted coffee residue (denoted as ECR), or called spent coffee ground, is inevitably generated from soluble coffee production during the extraction process, where the roasted and grinding coffee is introduced into percolators in countercurrent treatment with the pressurized hot water to extract the favors (soluble materials) in the soluble or instant coffee manufacturing factory [4]. The solid final product is thus obtained, and the insoluble residue (a slurry containing spent coffee grounds) is screw pressed. The residue weighs approximately 50% of the total input mass of coffee feedstock, representing a significant bioresource from the coffee-derived products processor. In Taiwan, for example, the annual generation of ECR from the food processors was estimated as over 6000 metric tons based on about 12,000 metric tons of imported coffee (not roasted and not decaffeinated) in 2009. Because of its high organic contents such as carbohydrate, protein, fiber, caffeine, polyphenols, tannins, and pectins, ECR was suitable as an animal feed, soil conditioner, and organic fertilizer [5], or further reused as a potential feedstock to produce useful products such as enzymes, organic acids, flavours and aroma compounds [6]. On the other hand, ECR is characterized chemically by a high content of carbon source. In this respect, it is

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0165-2370/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jaap.2011.09.010

similar to various agricultural processing by-products used as good biomass fuels in residentials and mills [2].

However, the use of raw biomass residue as a fuel often faces several problems, which may limit its wider application in the power generation. These include large bulk volume, high moisture content, low heating value and energy density, hygroscopic nature, and smoke during combustion, making it low in combustion efficiency [7,8]. In view of overcoming some of the aforementioned limitations of biomass material, thermochemical conversion is a promising route to convert lignocellulosic biomass to fuel, chemical, and renewable power [9]. Pyrolysis is generally described as the thermal decomposition of the organic components (long polysaccharides) in biomass in an inert atmosphere at mediate temperature to yield biochar (charcoal). As a result, this process improves the thermochemical properties of biomass, and produces a hydrophobic solid product with an increased energy density.

In view of reusing ECR as a biomass precursor for the production of pyrolysis products, several research works have been performed on this [10–15]. However, these focused on the preparation of activated carbon using chemical and physical activation. Although a few studies paid attention to the use of coffee husk (another coffee residue) as an energy source [16,17], very little work on the pyrolysis of ECR is available in the published literature. Data on the fuel properties (especially in true density) of resulting biochars are also limited. In this study, the thermochemical characteristics of ECR were investigated using the standard methods. Then, the pyrolysis of ECR was studied in a tubular fixed-bed system. A series of biochar products were thus prepared at the heating rate of about 10 K/min up to the prescribed temperature (i.e., 673–973 K), and further analyzed using chemical and physical techniques to determine its possibility of being a potential source of renewable fuels.

2. Materials and methods

2.1. Materials

The biomass sample used as the feedstock for its characteristic analysis and experimental pyrolysis runs was exhausted coffee residue (denoted as ECR), which was obtained from a local soluble coffee factory in southern Taiwan. This bioresource sample was first closely stored in grass bottles. Prior to the thermochemical characteristics analyses and pyrolysis experiments, each prepared sample was dried at about 373 K for at least 24 h.

2.2. Thermochemical characteristics analyses of exhausted coffee residue

2.2.1. Proximate analysis

According to the American Society for Testing and Materials (ASTM) Standard Test Methods, the analysis was carried out to determine the proximate properties (i.e., moisture, volatile matter, ash, and fixed carbon) in the ECR sample. In order to evaluate the precision of measurement, each sample was repeatedly carried out in triplicate. Common alkali/alkaline earth and other inorganic elements in ECR were further analyzed by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) described below.

2.2.2. Chemical structure analysis

The chemical structure analysis in the ECR sample was determined according to the Chinese National Standards (CNS) methods: the Method of Test for Holocellulose in Wood (CNS 3085) and the Method of Test for Acid-insoluble Lignin in Wood (CNS 14907).

2.2.3. Ultimate (elemental) analysis

The organic elements (i.e., carbon, hydrogen, nitrogen, oxygen, and sulfur) analyses of the ECR sample (2–3 mg) were conducted by using an elemental analyzer (Model: vario EL III; Elementar Co., Germany). For each analysis, the standard samples (i.e., sulfanilic acid and benzoic acid) were first analyzed for checking the experimental error within ±1% for C/H/N/S elements and O element, respectively.

2.2.4. Calorific value analysis

The higher heating value (HHV), also called gross calorific value, was measured with an adiabatic oxygen bomb calorimeter (Model: CALORIMETER ASSY 6200; Parr Instrument Co., USA). In the experiments, about 0.5 g of the dried ECR was conducted in the calorimeter to measure the constant volume heat released by the combustion of the biomass with pure oxygen.

2.2.5. Trace element analysis

An ICP-AES (Model: JY2000-2; HORIBA Jobin-Yvon Co., France) was used to determine the 19 relevant elements, including Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, P, Pb, Se, Si, Ti, and Zn. Prior to analysis, the ECR sample (about 0.2–0.5 g) was first digested by the concentrated nitric acid/hydrogen peroxide/hydrogen fluoride (3:1:0.5 by volume) solutions in a pressure bomb at 170 °C for 6 h to form the homogeneous solution samples. The resulting digested solution was diluted with deionized water to 50 dm^3, in which 2–3 dm^3 diluted solution was taken out to measure its inorganic contents.

2.3. Pyrolysis experiments

Although several operating parameters during the pyrolysis process contribute to the characterization of resulting biochar, the treatment temperature is expected to be the most important factor because the thermochemical changes (e.g., the release of volatiles and condensable compounds from the unorganized phase of the biomass) are all temperature dependent [18]. Thus, the temperature parameter was only considered in the present study. The biochar products were prepared from the pyrolysis of the ECR sample in a vertically fixed-bed reactor as reported previously [19,20]. For all experiments, the mass (10 g, in each set of experiments) of the sample was placed into a net stainless steel holder, and then housed at the center of the tubular reactor. The sweep gas from a nitrogen cylinder at a constant flow rate of 500 cm^3/min was precisely metered to the experimental system using a mass flow controller. The experimental conditions in the pyrolysis system were performed at the fixed heating rate of about 10 K/min up to the prescribed temperature ranging from 673 to 973 K, and then held for 1 h before cooling to room temperature. The resulting biochar product was taken from holding crucible in order to weigh its mass. The yields (burn-off levels) of the resulting products were thus calculated based on the difference between the masses before and after pyrolysis. In order to evaluate the availability of biochar products as solid fuels, their typical fuel properties were further measured as previously described in Section 2.2.

2.4. Fuel property analysis of resulting biochar

2.4.1. Thermochemical property analysis

For a preliminary analysis, the thermochemical property analyses (including proximate analysis, ultimate analysis and calorific value) in the typical biochar sample were determined according to the standard methods as previously described in Section 2.2.

2.4.2. True density

The true density (or called helium-based solid density) is defined as the ratio of the sample mass to the volume occupied by that mass [21]. In the measurement of true density, the contribution to the volume of pores or internal voids must be subtracted according to

Table 1
Proximate, elemental and chemical structure analyses of ECR sample.

Property	Value[a]
Proximate analysis[b]	
Moisture (wt%)	11.52 ± 0.43
Volatile (wt%)	79.52 ± 0.01
Ash (wt%)	0.73 ± 0.20
Fixed carbon[c] (wt%)	8.23
Ultimate analysis[d]	
Carbon (wt%)	52.54 ± 0.43
Hydrogen (wt%)	6.95 ± 0.03
Oxygen (wt%)	34.82 ± 0.10
Nitrogen (wt%)	3.46 ± 0.01
Sulfur (wt%)	0.10 ± 0.00
Chemical structure[d]	
Holocellulose (wt%)	47.2 ± 0.2
Lignin (wt%)	39.4 ± 0.5
Calorific value (MJ/kg)	23.5 ± 0.0

[a] The mean ± standard deviation for two/three determinations.
[b] Air-dry basis (as received sample).
[c] By difference.
[d] On a dry basis.

its definition. In this regard helium is the most used gas because it can penetrate even the very small pores in the powder sample because of its extreme inertness (avoid being adsorbed) and very small molecule size (about 0.2 nm). A helium displacement method with a pycnometer (Micromeritics Co., USA; Model No.: AccuPyc 1340) was used to measure the true density (ρ_s) of the biochar sample in this work.

3. Results and discussion

3.1. Characterization of exhausted coffee residue

The data in Table 1 indicated the results of proximate, ultimate, and chemical composition analyses for ECR. It is evident that the biomass comprises a large percentage of volatile matter (i.e., 79.52 wt%). The contents of fixed carbon and ash in the sample are only 8.23 and 0.73 wt%, respectively. It is well known that fixed carbon is the solid combustible residue that remains after a particle sample is heated and the volatile matter is expelled. Thus, it is used as an estimate of the amount of coke that will be yielded from a solid fuel sample. Further, the ash content in ECR is relatively lower than those contents in common biomass fuels [2]. For example, the ash contents of rice hull and corn cob are about 17.9 and 1.4 wt%, respectively, on a dry basis.

The ultimate analyses and structural compositions in Table 1 revealed the high contents of carbon and oxygen in ECR, indicating the lignocellulosic structure of this agricultural residue. In addition, the content of cellulose (holocellulose) is more than that of lignin for the biomass sample. On the other hand, the molar ratio of hydrogen to carbon (H/C) is 1.67 for cellulose, $(C_6H_{10}O_5)_n$, and 1.60 for hemicellulose, $(C_5H_8O_4)_n$. In this regard, the molar ratio of H/C for the ECR sample is about 1.59, suggesting that the major organic constituents are cellulose and hemicellulose as shown in Table 1. However, it should be noted that the content (about 3.5 wt%) of nitrogen in ECR are relatively high in comparison with those (below 1 wt%) of most of energy crops and fossil fuels [2]. As a result, the fuel-bound nitrogen will contribute to nitrogen oxides (NO_x) emission from biomass combustion. As in common biomass fuels, there is less than detectable amount of sulfur in ECR. It should be therefore expected that sulfur oxides (SO_x) would not be emitted in a large extent.

From the data in Table 1, ECR is chemically characterized by high contents (i.e., 52.54 and 6.95 wt%, respectively) of carbon and hydrogen, and low content of ash (i.e., 0.73 wt%). Therefore, its heating value is relatively high up to around 23.5 MJ/kg-dried basis as shown in Table 1. In this respect, it is very similar to various other agricultural by-products [2]. It means that the dried ECR can be directly utilized by residential, industrial and energy sectors as an available energy source for cooking, for heating, for co-firing, or for generation of electricity using a stream turbine, an internal combustion engine, or gas turbine [22]. Like coffee husk briquettes [17], ECR can be further compressed as briquette or pellet products to increase its energy density and to lower the emissions of air pollutants from the combustion process. Also due to its very low contents of mercury and chlorine in ECR [23], co-firing of coal and ECR may be an environmentally friendly control strategy for CO_2, SO_x and mercury abatement in coal-fired power generation.

Table 2
Contents of relevant trace elements of ECR sample.

Inorganic element (wt%)	Value[a]	Method detection limit (ppm)
K	0.403 ± 0.038	–
Mg	0.143 ± 0.001	–
P	0.112 ± 0.002	–
Ca	0.103 ± 0.001	–
Ag	ND	2.4
Al	ND	7.7
As	ND	48.4
Ba	ND	0.2
Cd	ND	3.3
Cr	ND	6.0
Cu	ND	3.8
Fe	ND[b]	4.5
Na	ND	12.7
Ni	ND	8.4
Pb	ND	13.3
Se	ND	45.1
Si	ND	50.1
Ti	ND	2.0
Zn	ND	1.1

[a] The mean ± standard deviation for three determinations on a dry basis.
[b] Not detectable.

Another thermochemical property, which influences the design of biomass-to-energy conversion facilities, is inorganic elements in ECR. These for 19 elements are listed in Table 2, showing that the biomass has substantially smaller concentrations of Al, As, Ba, Cd, Cr, Cu, Fe, Na, Ni, Pb, Se, Si, Ti, and Zn. However, the macronutrients Ca, K, Mg and P are moderately high in ECR, which is consistent with recent findings on mineral composition and ash content analyses for six major energy crops [24]. These inorganic elements could be present in oxide forms such as K_2O, CaO, P_2O_5 and MgO that are easily volatilized during combustion and then deposited on the heat transfer surface of boiler [25].

3.2. Yields of biochar products

The thermal decomposition of ECR under the pyrolysis temperatures produces mainly three products: solid biochar product which retains most of the energy content of the feedstock, condensable liquid including moisture, carboxylic acids and other oxygenates, and non-condensable gases [7]. The last two products can be represented by volatiles. Generally, the total yield of volatiles increases with raising pyrolysis temperature. This result is attributable to the competition between charring and devolatilization reactions, occurring in an inert atmosphere at moderate temperature (>673 K) [18].

In view of the aforementioned, the experimental pyrolysis conditions in the present study were performed at the heating rate of about 10 K/min up to the prescribed temperature ranging from 673 to 973 K. The yields of the resulting biochar products are in the range of 25–40 wt%, listed in Table 3. The yield was observed to decrease slightly at higher pyrolysis temperature, which should

Table 3
Calorific values and yields of resulting biochar products.

Biochar sample	Heating rate[a] (K/min)	Yield[a] (%)	Calorific value[b] (MJ/kg)
C-Biochar-673[c]	7.3 ± 0.2	38.6 ± 0.5	31.9 ± 0.5
C-Biochar-773[c]	9.6 ± 0.2	29.8 ± 1.4	30.5 ± 0.4
C-Biochar-873[c]	10.0 ± 0.1	28.0 ± 1.1	30.6 ± 0.4
C-Biochar-973[c]	10.1 ± 0.1	26.6 ± 1.2	30.4 ± 0.3

[a] The mean ± standard deviation for three determinations.
[b] The mean ± standard deviation for four determinations on a dry basis.
[c] The resulting biochar products was prepared at the pyrolysis temperature of 673, 773, 873, and 973 K, respectively.

be attributed to the volatilization of tar products derived from the lignocellulosic components of ECR.

3.3. *Fuel properties of biochar products*

From the standpoint of energy use of biochar in replacement of coal, its heating value is the most important fuel property. From the data in Table 3, it can be seen that the calorific value of biochar from ECR (e.g., 31.9 MJ/kg for C-Biochar-673) was relatively high as compared to that (i.e., 28.0–32.0 MJ/kg) of fossil coal [22]. Furthermore, the pyrolysis temperature of 673 K was found to be optimal for the higher calorific values presented in this study. Interestingly, there was no obvious change on the calorific value of resulting biochar at the higher temperature ranging from 773 K to 973 K. As compared to the calorific value of ECR (23.5 MJ/kg, listed in Table 1) an increase of 36% was obtained for the resulting biochar. The experimental results have demonstrated that the biochar derived from ECR may be used as a fuel charcoal high in energy content and organic carbon.

It is well known that the thermochemical property of solid fuel is defined in terms of its proximate and ultimate (elemental) analyses. As a preliminary demonstration, the chemical composition of a resulting biochar was determined. In the proximate analysis, the volatile matter, ash, and fixed carbon of C-Biochar sample are about 12, 23 and 65 wt% on a dry basis, respectively. On the other hand, the ultimate analysis was found to be around 80, 3, 5, 0 and 12 wt% for carbon, hydrogen, nitrogen, sulfur and oxygen within the C-Biochar sample. These analyses showed that the ECR-based biochar is very similar to the commercial coal. In contrast to its environmental and energy benefits, corrosive elements in ECR-based biochar could be released to the atmosphere during combustion. In this regard, the content of nitrogen in the biochar is relatively high, about 5% by weight in comparison with most of coals having nitrogen contents below 2 wt% [26]. It should be noted that fuel-bound nitrogen would contribute to nitrogen oxides (NO_x) emission from biomass combustion facilities where they could have a need for installing NO_x control systems.

The mechanical strength of biochar, which is a characteristic for the ability to withstand wear and attrition during use, is related to its true density. It means that the increased molecular order of biochar will give it a higher mechanical strength than the biomass feedstock from which it was derived [18]. A graph (Fig. 1) of true density vs. temperature showed that the conversion of low-density disordered carbon to higher-density turbostratic carbon, which was consistent with the finding by Brown et al. [27]. In the case of resulting biochars from the pyrolysis of ECR, the values of the true densities (i.e., 1.520 ± 0.009, 1.720 ± 0.019, 1.843 ± 0.023 and 2.030 ± 0.038, respectively, for ten measurements) proportionally increased with increase in the process temperature (i.e., 673, 773, 873 and 973 K, respectively). The higher temperature seemed to lead to the increase in true density of resulting biochar. The peak occurs at above 973 K is probably associated with the active pyrolysis of the cellulosic fragments and the condensation (or shrinkage) processes which result in an increased content of aromatic carbon clusters. In the present study, the maximum true density was found to be around 2.0 g/cm^3 in the organized phase of resulting biochar formed by graphite-like crystallites. Such value is only slightly below the density of solid graphite of 2.25 g/cm^3. It should be noted that the maximum density of carbon in biochars has been reported to lie between 2.0 and 2.1 g/cm^3 based on X-ray measurements [28]. As suggested by Brown et al. [27], the true density may serve as an approximate indicator of the highest pyrolysis temperature, regardless of the exact thermal history such as heating rate.

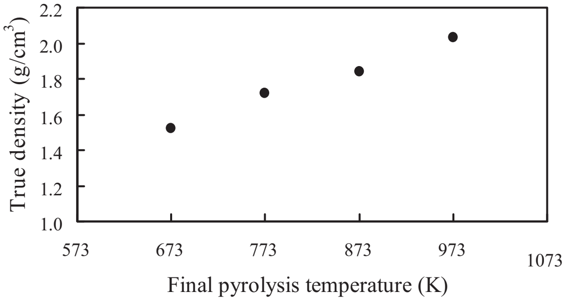

Fig. 1. Helium-based solid density (true density) of resulting biochar as a function of pyrolysis temperature.

4. Conclusions

The reuse of the coffee milling by-products as energy sources has received much attention in recent years due to the economic consideration, energy crisis and environmental issue. In this work, the thermochemical characteristics of exhausted coffee residue (ECR) have been analyzed according to the standard methods. The results showed that molar ration of hydrogen to carbon (H/C) for the biomass was about 1.59, which is relatively low in comparison with those (2.2–2.4) of hydrocarbon fuels, but are close to the cellulose (H/C = 1.67) and hemicellulose (H/C = 1.60). In order to greatly improve the thermochemical and fuel properties of ECR, the pyrolysis treatment was performed at the temperature of 673–973 K and the heating rate of about 10 K/min, yielding a series of biochar products with high carbon (>80%), fixed carbon (>60%) and calorific value (>30.1 MJ/kg). The calorific value of the optimal biochar from ECR (e.g., 31.9 MJ/kg) was relatively high as compared to that (i.e., 28.0–32.0 MJ/kg) of coal. On the other hand, the biochars were characterized using helium-based solid density (true density), showing that the density increased with increasing pyrolysis temperature in accord with the conversion of low-density disordered carbon to high-density turbostratic carbon. The experimental results have demonstrated that the biochar derived from ECR may be used as a solid fuel in the industrial sector.

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